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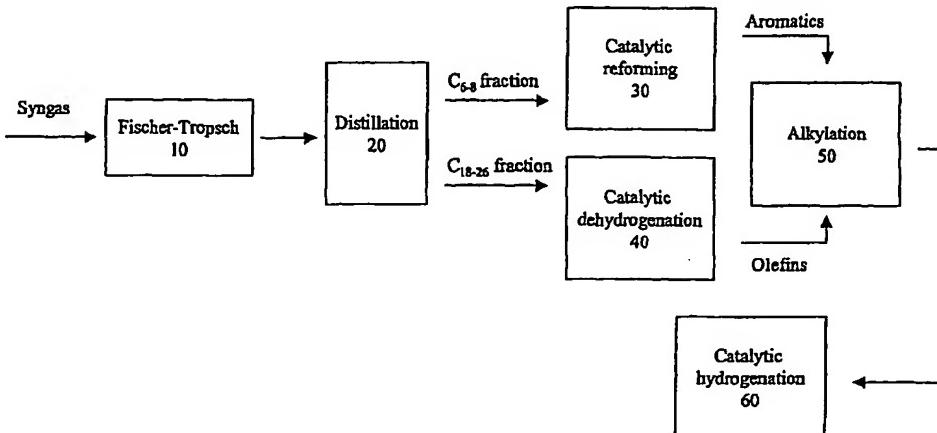
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(54) Title: SYNTHESIS OF ALKYLBENZENES AND SYNLUBES FROM FISCHER-TROPSCH PRODUCTS



**WO 01/64610 A1**

(57) Abstract: An integrated process for producing alkylbenzenes, sulfonated alkylbenzenes and/or alkylcyclohexanes from syngas is disclosed. The process involves subjecting syngas to Fischer-Tropsch conditions. Fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons are isolated from the resulting product stream. The C<sub>6-8</sub> fraction is subjected to catalytic reforming conditions to form aromatics. The C<sub>18-26</sub> fraction may include sufficient olefins for use in an alkylation reaction with the aromatics. Optionally, the fraction may be subjected to dehydrogenation conditions to provide additional olefins. The resulting olefins are reacted with the aromatics in an alkylation reaction to yield alkylbenzenes. Unconverted olefins, paraffins, and aromatics can be obtained from the product stream via fractional distillation and recycled to form additional products. The alkylbenzenes can be hydrogenated to yield alkylcyclohexanes, which are useful as synlubes or as components in lube oil compositions. Alternatively, the alkylbenzenes can be sulfonated, and the resulting sulfonated alkylbenzenes used, for example, as detergents and/or dispersants.

**WO 01/64610 A1**



*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

-1-

1                   SYNTHESIS OF ALKYLBENZENES AND SYNLUBES  
2                   FROM FISCHER-TROPSCH PRODUCTS

3

4                   BACKGROUND OF THE INVENTION

5

6     There is a large demand for alkylbenzenes and synthetic lubricants  
7     (synlubes). Alkylbenzenes are often used as detergents in a variety of  
8     applications, for example, as lubricant oils. The preferred alkylbenzenes have  
9     linear (as opposed to branched) alkyl groups, and are referred to as linear  
10    alkylbenzenes. Linear alkylbenzenes are preferred over branched  
11    alkylbenzenes because of their relatively high rate of biodegradability.

12

13    Currently, these products are prepared by alkylating normal alpha olefins  
14    (NAOs), or isomerized olefins derived from normal alpha olefins, with benzene  
15    or toluene. The NAOs are typically made from ethylene, which is a relatively  
16    expensive raw material. Accordingly, the cost of the alkylbenzenes and  
17    synlubes is relatively high. NAOs can also be prepared by wax cracking and  
18    by modified ethylene oligomerization processes.

19

20    Linear alkylbenzenes can also be prepared from high purity unbranched  
21    paraffins by dehydrogenating the paraffins to form olefins, and then alkylating  
22    aromatic rings with the olefins. However, this approach is limited by the  
23    relatively high cost of the paraffinic starting material and the limited supply of  
24    high quality unbranched paraffins. If the paraffins are not extremely pure, but  
25    rather, include isoparaffins or naphthenes, the catalysts tend to foul and the  
26    products tend not to perform adequately.

27

28    One type of synthetic lubricant is derived from 1-decene that has been  
29    trimerized and hydrogenated to form a T-shaped C<sub>30</sub> isoparaffin. The  
30    particular shape of the molecule provides it with a relatively high viscosity  
31    index and low pour point, which is desirable for synthetic lubricants. However,  
32    the decene trimer is not unique. Many alkylcyclohexanes also have relatively

-2-

1 high viscosity indexes (VI's) and low pour points (Briant et al., "Rheological  
2 properties of lubricants", Editions Tecnicp (Chapter 7 (1989)).

3

4 It would be desirable to provide additional methods for forming alkylbenzenes  
5 and alkylcyclohexanes. The present invention provides such methods.

6

7 SUMMARY OF THE INVENTION

8

9 In its broadest aspect, the present invention is directed to an integrated  
10 process for preparing alkylbenzenes, sulfonated alkylbenzenes and/or  
11 alkylcyclohexanes from syngas. In the first step, syngas is reacted under  
12 Fischer-Tropsch conditions to form one or more product streams that include  
13 C<sub>6-8</sub> and C<sub>18-26</sub> fractions. These fractions can be isolated, for example, via  
14 conventional fractional distillation. Both fractions are optionally but preferably  
15 treated, for example, by hydrotreating or extraction, to remove oxygenates  
16 and other by-products of the Fischer-Tropsch synthesis.

17

18 The C<sub>6-8</sub> fraction can be converted to aromatics via catalytic reforming  
19 chemistry, preferably using the AROMAX® Process. The C<sub>6-8</sub> fraction is ideal  
20 for use in the AROMAX® Process, because it tends to have low levels of  
21 sulfur, a known poison for the catalyst used in the AROMAX® Process.

22

23 The C<sub>18-26</sub> fraction tends to be highly linear, and also has low levels of  
24 impurities known to adversely affect processes for alkylating aromatics with  
25 olefins. Depending on the particular Fischer-Tropsch conditions, the fraction  
26 may include sufficient olefins and alcohols such that it can be directly reacted  
27 with aromatics to form alkylbenzenes. The aromatics and C<sub>18-26</sub> hydrocarbons  
28 used to form the alkylbenzenes can be derived exclusively from the C<sub>6-8</sub> and  
29 C<sub>18-26</sub> fractions from the Fischer-Tropsch reaction, or can optionally be  
30 combined with aromatics and/or C<sub>18-26</sub> hydrocarbons from other feedstocks,

-3-

1 assuming that the other feedstocks do not include impurities that would have  
2 a detrimental effect on the subsequent chemistry.

3

4 The paraffinic portion of the C<sub>18-26</sub> fraction can be dehydrogenated to form  
5 olefins and reacted with the aromatics. The alkylbenzenes can be used, for  
6 example, as lubricant oils, or can be sulfonated to form detergents.

7

8 The alkylbenzenes can be reduced to form alkylcyclohexanes. In one  
9 embodiment, the hydrogen produced during the catalytic reforming chemistry  
10 can be used to hydrogenate the alkylbenzenes to form the alkylcyclohexanes.  
11 The resulting alkylcyclohexanes can be used, for example, as synlubes or as  
12 a component in synlube compositions. Preferably, the lubricant compositions,  
13 including the alkylbenzenes and/or alkylcyclohexanes, also include  
14 conventional lubricant additives.

15

16 In one embodiment, the Fischer-Tropsch chemistry is performed in two  
17 separate reactors, in order to maximize the relative amounts of C<sub>6-8</sub> and C<sub>18-26</sub>  
18 fractions. The first reactor can be set up using conditions in which chain  
19 growth probabilities are relatively low to moderate, and the product of the  
20 reaction includes a relatively high proportion of low molecular (C<sub>2-8</sub>) weight  
21 olefins and a relatively low proportion of high molecular weight (C<sub>30+</sub>) waxes.  
22 This set of conditions optimizes yields of the C<sub>6-8</sub> fraction used to form the  
23 aromatic rings which are to be alkylated with the C<sub>18-26</sub> paraffins. Preferred  
24 catalysts are iron-containing catalysts.

25

26 The second reactor can be set up using conditions in which chain growth  
27 probabilities are relatively high, and the product of the reaction includes a  
28 relatively low proportion of low molecular (C<sub>2-8</sub>) weight olefins and a relatively  
29 high proportion of high molecular weight (C<sub>30+</sub>) waxes. Preferred catalysts  
30 are cobalt-containing catalysts. This set of conditions optimizes yields of the  
31 C<sub>18-26</sub> fraction used to alkylate the aromatic rings.

32

1                   BRIEF DESCRIPTION OF THE DRAWINGS

2

3   Figure 1 is a schematic flow diagram representing one embodiment of the  
4   invention.

5

6                   DETAILED DESCRIPTION OF THE INVENTION

7

8   The present invention is directed to an integrated process for producing  
9   alkylbenzenes, sulfonated alkylbenzenes and/or alkylcyclohexanes from  
10   syngas. As used herein, the term "integrated process" refers to a process  
11   comprising a sequence of steps, some of which may be parallel to other steps  
12   in the process, but which are interrelated or somehow dependent upon either  
13   earlier or later steps in the total process.

14

15   Fischer-Tropsch chemistry is used to convert the syngas to a product stream  
16   which includes a C<sub>6-8</sub> fraction and a C<sub>18-26</sub> fraction. The Fischer-Tropsch  
17   chemistry provides products which are highly linear and which include low  
18   levels of sulfur. The C<sub>6-8</sub> fraction is subjected to catalytic reforming conditions  
19   for form C<sub>6-8</sub> aromatics. The C<sub>18-26</sub> fraction is dehydrogenated to form C<sub>18-26</sub>  
20   olefins, which are used to alkylate the C<sub>6-8</sub> aromatics. The aromatics and  
21   C<sub>18-26</sub> hydrocarbons used to form the alkylbenzenes can be exclusively from  
22   the Fischer-Tropsch reaction, or can optionally be combined with aromatics  
23   and/or C<sub>18-26</sub> hydrocarbons from other feedstocks. The resulting  
24   alkylbenzenes can be used directly, or can be sulfonated to form sulfonated  
25   alkylbenzenes or hydrogenated to form alkylcyclohexanes.

26

27                   Fischer-Tropsch Chemistry

28

29   In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by  
30   contact with a Fischer-Tropsch catalyst under reactive conditions. Depending  
31   on the quality of the syngas, it may be desirable to purify the syngas prior to  
32   the Fischer-Tropsch reactor to remove carbon dioxide produced during the

-5-

1 syngas reaction and any sulfur compounds, if they have not already been  
2 removed. This can be accomplished, for example, by contacting the syngas  
3 with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a  
4 packed column.

5

6 Examples of conditions for performing Fischer-Tropsch type reactions are well  
7 known to those of skill in the art. Suitable conditions are described, for  
8 example, in U.S. Patent Nos. 4,704,487, 4,507,517, 4,599,474, 4,704,493,  
9 4,709,108, 4,734,537, 4,814,533, 4,814,534 and 4,814,538, the contents of  
10 each of which are hereby incorporated by reference in their entirety.

11

12 In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on  
13 a metal oxide support. The catalysts may also contain a noble metal  
14 promoter(s) and/or crystalline molecular sieves. Certain catalysts are known  
15 to provide chain growth probabilities that are relatively low to moderate, and  
16 the reaction products include a relatively high proportion of low molecular  
17 (C<sub>2-8</sub>) weight olefins and a relatively low proportion of high molecular weight  
18 (C<sub>30+</sub>) waxes. Certain other catalysts are known to provide relatively high  
19 chain growth probabilities, and the reaction products include a relatively low  
20 proportion of low molecular (C<sub>2-8</sub>) weight olefins and a relatively high  
21 proportion of high molecular weight (C<sub>30+</sub>) waxes. Such catalysts are well  
22 known to those of skill in the art and can be readily obtained and/or prepared.  
23 The product in the C<sub>18-26</sub> range may include sufficient olefins and alcohols for  
24 use in alkylation reactions with aromatics, depending on the Fischer-Tropsch  
25 conditions. For example, Fischer-Tropsch reactions using an iron catalyst  
26 and run at a relatively high temperature tend to provide a C<sub>18-26</sub> fraction that  
27 includes a sufficient amount of olefins for the alkylation reaction.

28

-6-

1                   Catalyst Selection

2                   Catalysts with low chain growth probabilities

3

4   In order to provide a product stream from a Fischer-Tropsch reaction including  
5   a relatively large C<sub>6-8</sub> fraction, any catalyst that provides relatively low to  
6   moderate chain growth probabilities can be used. Typically, catalysts with an  
7   alpha value between about 0.600 and 0.700 provide low chain growth  
8   probabilities. Catalysts with an alpha value between about 0.700 and 0.800  
9   provide moderate chain growth probabilities. Preferable catalysts are those  
10   which tend to provide high yields (i.e., greater than about 20 and more  
11   preferably greater than about 30 percent by weight of the products other than  
12   methane) of light (C<sub>2-8</sub>) alpha olefins.

13

14   Preferred catalysts are iron-containing catalysts. Iron itself can be used and,  
15   when iron oxides are formed, can be reduced with hydrogen back to iron.  
16   However, because the presence of iron fines in the product stream is not  
17   preferred, and because iron oxides (rust) decrease the surface area of the  
18   catalyst available for reaction, other iron-containing catalysts may be  
19   preferred. Examples of suitable iron-containing catalysts include those  
20   described in U.S. Patent No. 4,544,674 to Fianto et al. and Xu et al., pp. 47-53,  
21   *Chemtech* (Jan. 1998).

22

23   In a preferred embodiment, the iron catalysts include at least about 10 to  
24   about 60 weight percent iron. More preferably, they include between about 20  
25   to about 60 weight percent iron, and most preferably about 30 to about  
26   50 weight percent iron. These catalysts can be unsupported, but are  
27   preferably promoted with a refractory metal oxide (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.), alkali (K,  
28   Na, Rb) and/or Group IB metals (Cu, Ag). These catalysts are usually  
29   calcined, but usually are not reduced. Rather, they are brought up to reaction  
30   temperature directly in the CO/H<sub>2</sub> feed.

31

1 Co-precipitated iron-based catalysts, including those containing cobalt, can be  
2 used. High levels of cobalt in an iron-cobalt alloy are known to produce  
3 enhanced selectivity to olefinic products, as described, for example, in Stud.  
4 Surf. Sci. Catal. 7, Pt/A, p. 432 (1981).

5

6 Examples of co-precipitated iron-cobalt catalysts and/or alloys include those  
7 described in U.S. Patent Nos. 2,850,515, 2,686,195, 2,662,090, and  
8 2,735,862; AIChE 1981 Summer Nat'l Meeting Preprint No. 408, "The  
9 Synthesis of Light Hydrocarbons from CO and H<sub>2</sub> Mixtures over Selected  
10 Metal Catalysts", ACS 173rd Symposium, Fuel Division, New Orleans, March  
11 1977; *J. Catalysis* 1981, No. 72(1), pp. 37-50; Adv. Chem. Ser. 1981, 194,  
12 573-88; Physics Reports (Section C of Physics Letters) 12 No. 5 (1974)  
13 pp. 335-374; UK patent application No. 2050859A; *J. Catalysis* 72, 95-110  
14 (1981); Gmelins Handbuch der Anorganische Chemie 8, Auflage (1959),  
15 pg. 59; *Hydrocarbon Processing*, May 1983, pp. 88-96; and *Chem. Ing. Tech.*  
16 49 (1977) No. 6, pp. 463-468.

17

18 Methods for producing high surface area metal oxides are described, for  
19 example, in the French article, "C. R. Acad. Sc. Paris", p. 268 (28 May 1969)  
20 by P. Courte and B. Delmon. Metal oxides with a high surface area are  
21 prepared by evaporating to dryness aqueous solutions of the corresponding  
22 glycolic acid, lactic acid, malic or tartaric acid metal salts. One oxide that was  
23 prepared was CoFe<sub>2</sub>O<sub>4</sub>.

24

25 Iron-cobalt spinels which contain low levels of cobalt, in an iron/cobalt atomic  
26 ratio of 7:1 to 35:1, are converted to Fischer-Tropsch catalysts upon reduction  
27 and carbiding (see, for example, U.S. Patent No. 4,544,674 to Faito et al.).  
28 These catalysts tend to exhibit high activity and selectivity for C<sub>2</sub>-C<sub>6</sub> olefins  
29 and low methane production.

30

31 The contents of each of the patents and publications referred to above are  
32 hereby incorporated by reference.

1                   Catalysts with High Chain Growth Probabilities

2

3   In order to provide a product stream from a Fischer-Tropsch reaction including  
4   a relatively large C<sub>18-26</sub> fraction, any catalyst that provides relatively high chain  
5   growth probabilities can be used. Preferably, the catalyst used in the second  
6   stage is a cobalt-containing catalyst. Ruthenium is also an effective  
7   Fischer-Tropsch catalyst, but is more expensive.

8

9   One suitable cobalt catalyst that can be used is described in U.S. Patent  
10   No. 4,579,986, as satisfying the relationship:

11

12                    $(3 + 4R) > L/S > (0.3 + 0.4R)$ ,

13

14   wherein:

15

16                   L = the total quantity of cobalt present on the catalyst, expressed as  
17                   mg Co/ml catalyst;

18                   S = the surface area of the catalyst, expressed as m<sup>2</sup>/ml catalyst; and

19                   R = the weight ratio of the quantity of cobalt deposited on the catalyst  
20                   by kneading to the total quantity of cobalt present on the catalyst.

21

22   Other suitable catalysts include those described in U.S. Patent  
23   Nos. 4,077,995, 4,039,302, 4,151,190, 4,088,671, 4,042,614 and 4,171,320.  
24   U.S. Patent No. 4,077,995 discloses a catalyst that includes a sulfided mixture  
25   of CoO, Al<sub>2</sub>O<sub>3</sub> and ZnO. U.S. Patent No. 4,039,302 discloses a mixture of the  
26   oxides of Co, Al, Zn and Mo. U.S. Patent No. 4,151,190 discloses a metal  
27   oxide or sulfide of Mo, W, Re, Ru, Ni or Pt, plus an alkali or alkaline earth  
28   metal, with Mo-K on carbon being preferred.

29

30   U.S. Patent No. 4,088,671 discloses minimizing methane production by using  
31   a small amount of ruthenium on a cobalt catalyst. Supported ruthenium

-9-

1 catalysts suitable for hydrocarbon synthesis via Fischer-Tropsch reactions are  
2 disclosed, for example, in U.S. Patent Nos. 4,042,614 and 4,171,320.

3

4 In general, the amount of cobalt present in the catalyst is between about 1  
5 and about 50 weight percent of the total catalyst composition, more preferably  
6 between about 10.0 and 25 weight percent.

7

8 Preferably, the catalyst contains between about 3 and 60 ppw cobalt, between  
9 0.1 and 100 ppw of at least one of zirconium, titanium or chromium per  
10 100 ppw of support (typically, silica, alumina, or silica-alumina and mixtures  
11 thereof).

12

## Catalyst Supports

14

15 The type of support used can influence methane production. Suitable metal  
16 oxide supports or matrices which can be used to minimize methane  
17 production include alumina, titania, silica, magnesium oxide, alkaline earth  
18 titanates, alkali titanates, rare earth titanates and mixtures thereof.

19

20 Methane production can be decreased using supported ruthenium catalysts.  
21 Titania or titania-containing supports provide lower methane production than  
22 for example, silica, alumina or manganese oxide supports. Accordingly,  
23 titania and titania-containing supports are preferred.

24

25 Typically, the catalysts have a particle size of between 10 and 110 microns,  
26 preferably between 20 and 80 microns, more preferably between 25 and  
27 65 microns, and have a density of between 0.25 and 0.9 g/cc, preferably  
28 between 0.3 and 0.75 g/cc. The catalysts typically include one or more of the  
29 above-mentioned catalytic metals, preferably including iron in the first stage  
30 and cobalt in the second stage, on one of the above-mentioned catalyst  
31 supports. Preferably, the cobalt-containing catalysts include about 10 to  
32 14 percent cobalt on a low density fluid support, for example, alumina, silica

-10-

1 and the like, having a density within the ranges set forth above for the  
2 catalyst.

3

4 Promoters and Noble Metals

5

6 Methane selectivity is also influenced by the choice of promoter. Alkali metal  
7 promoters are known for reducing the methane selectivities of iron catalysts.  
8 Noble metals, such as ruthenium, supported on inorganic refractory oxide  
9 supports, exhibit superior hydrocarbon synthesis characteristics with relatively  
10 low methane production. Where a noble metal is used, platinum and  
11 palladium are generally preferred. Accordingly, alkali metal promoters and/or  
12 noble metals can be included in the catalyst bed of the first stage provided  
13 that they do not significantly alter the reaction kinetics from slow chain growth  
14 probabilities to fast chain growth probabilities.

15

16 The disclosures of each of the patents and articles discussed above are  
17 incorporated herein by reference in their entirety.

18

19 Operating Conditions

20

21 Fischer-Tropsch reactions designed to produce a relatively high proportion of  
22 the C<sub>6-8</sub> fraction are typically conducted at temperatures between about 270°C  
23 and 280°C, at a pressure of between about 1 and 20 ATM, in a slurry reactor  
24 or a fluidized bed reactor. Typical synthesis gas linear velocity ranges in the  
25 reactor are between about 2 and 40 cm per sec., preferably between about 6  
26 and 10 cm per sec.

27

28 The products of the Fischer-Tropsch reaction include methane, C<sub>2-5</sub>  
29 hydrocarbons, C<sub>6+</sub> hydrocarbons, water and carbon dioxide, as well as  
30 unreacted syngas. Water, methane, C<sub>2-5</sub> hydrocarbons and carbon dioxide  
31 are substantially removed to yield a product stream including mostly C<sub>6+</sub>

-11-

1 hydrocarbons. The C<sub>6+</sub> hydrocarbons are predominantly C<sub>6-8</sub> hydrocarbons,  
2 which tend to be roughly 75% by weight olefins, and 25% by weight paraffins.  
3 Optionally, but preferably, the product stream is hydrotreated at this stage to  
4 remove any oxygenated products. If desired, the C<sub>6-8</sub> hydrocarbons can be  
5 isolated, for example, via distillation.

6

7 Fischer-Tropsch reactions designed to produce a relatively high proportion of  
8 the C<sub>18-26</sub> fraction are typically conducted in either a fixed bed reactor or a  
9 slurry reactor, where slurry reactors are preferred. The operating temperature  
10 of the fixed bed reactor is between about 200°C and 225°C, and the operating  
11 temperature of the slurry reactor is between about 225°C and 250°C, with a  
12 temperature around 240°C preferred. Typical synthesis gas linear velocity  
13 ranges in the reactor are from about 2 to 40 cm per sec., preferably from  
14 about 6 to 10 cm per sec. The pressure is preferably between about 1 and  
15 30 ATM, with pressures between 20 and 30 ATM being particularly preferred.  
16 Above about 30 ATM, carbonyls may be formed and, therefore, pressures  
17 significantly above 30 ATM are not preferred. Further, the rate of reaction  
18 tends to increase with increased pressure, but tends to level off due to  
19 hydrodynamic problems at around 30 ATM.

20

21 The catalyst space velocities are typically between about 100 and  
22 10,000 cc/g/h, preferably between about 300 and 3,000 cc/g/h, for both  
23 stages.

24

25 The reaction mixture is preferably cooled to less than 100°C, and liquid  
26 products are trapped. Methane is preferably bled off to a syngas generator  
27 and recycled. Water is preferably removed.

28

29 The products of the Fischer-Tropsch reaction include methane, C<sub>2-50</sub>  
30 hydrocarbons, water and carbon dioxide, as well as unreacted syngas.  
31 Water, methane, C<sub>2-17</sub> hydrocarbons and carbon dioxide are substantially

-12-

1 removed to yield a product stream including mostly C<sub>18+</sub> hydrocarbons. The  
2 C<sub>18+</sub> hydrocarbons are mostly paraffinic. The desired C<sub>18-26</sub> fraction can be  
3 isolated, for example, by fractional distillation. Optionally, but preferably, the  
4 fraction is hydrotreated at this stage to remove any oxygenated products.

5

6 Of course, the Fischer-Tropsch chemistry can be performed using only one  
7 set of reaction conditions, and the C<sub>6-8</sub> and C<sub>18-26</sub> fractions can be isolated  
8 from the product mixture as described above.

9

10 As discussed above, slurry reactors can be preferred for either set of  
11 Fischer-Tropsch conditions. Bubble column slurry reactors can be particularly  
12 preferred. Details regarding bubble column slurry reactors can be found, for  
13 example, in Y. T. Shah et al., Design Parameters Estimations for Bubble  
14 Column Reactors, *AIChE Journal*, 28 No. 3 pp. 353-379 (May 1982);  
15 Ramachandran et al., Bubble Column Slurry Reactor, Three-Phase Catalytic  
16 Reactors, Chapter 10, pp. 308-332 Gordon and Broch Science Publishers  
17 (1983); Deckwer et al., Modeling the Fischer-Tropsch Synthesis in the Slurry  
18 Phase, *Ind. Eng. Chem. Process Des. Dev.* v 21, No. 2, pp. 231-241 (1982);  
19 Kölbel et al., The Fischer-Tropsch Synthesis in the Liquid Phase, *Catal.*  
20 *Rev.-Sci. Eng.*, v. 21(n), pp. 225-274 (1980); and U.S. Patent No. 5,348,982,  
21 the contents of each of which are hereby incorporated by reference in their  
22 entirety.

23

24 Since the catalyst metal may be present in the catalyst in the form of an oxide,  
25 the catalyst may be reduced with hydrogen prior to contact with the slurry  
26 liquid. The starting slurry liquid is typically a heavy hydrocarbon with a  
27 viscosity sufficient to keep the catalyst particles suspended (typically between  
28 4 and 100 centistokes at 100°C). The slurry liquid also has a low enough  
29 volatility to avoid vaporization during operation (typically an initial boiling point  
30 range of between about 350°C and 550°C). The slurry liquid is preferably  
31 essentially free of contaminants such as sulfur, phosphorous or chlorine

-13-

1 compounds. Initially, it may be desirable to use a synthetic hydrocarbon fluid  
2 such as a synthetic olefin oligomer as the slurry fluid.

3

4 Often, a paraffin fraction of the product having the desired viscosity and  
5 volatility is recycled as the slurry liquid. The slurry typically has a catalyst  
6 concentration of between about 2 and 40 percent catalyst, preferably between  
7 about 5 and 20 percent, and more preferably between about 7 and 15 percent  
8 catalyst based on the total weight of the catalyst, i.e., metal plus support.

9

10 Although the reactions described herein are described in terms of  
11 Fischer-Tropsch reactions, they can optionally be performed using various  
12 modifications of the literal Fischer-Tropsch process where hydrogen (or water)  
13 and carbon monoxide (or carbon dioxide) are converted to hydrocarbons  
14 (e.g., paraffins, ethers, etc.). Thus, the term Fischer-Tropsch type product or  
15 process is intended to apply to Fischer-Tropsch processes and products and  
16 the various modifications thereof and the products thereof. For example, the  
17 term is intended to apply to the Kolbel-Engelhardt process typically described  
18 by the reaction:

19



21

22                   The Separation of Product From the Fischer-Tropsch Reaction

23

24 The products from Fischer-Tropsch reactions generally include a gaseous  
25 reaction product and a liquid reaction product. The gaseous reaction product  
26 includes hydrocarbons boiling below about 650°F (e.g., tail gases through  
27 middle distillates). The liquid reaction product (the condensate fraction)  
28 includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil  
29 through heavy paraffins).

30

-14-

1 The minus 650°F product can be separated into a tail gas fraction and a  
2 condensate fraction, using, for example, a high pressure and/or lower  
3 temperature vapor-liquid separator or low pressure separators or a  
4 combination of separators. The condensate fraction includes about C<sub>5</sub> to C<sub>20</sub>  
5 normal paraffins and higher boiling hydrocarbons.

6

7 The fraction boiling above about 650°F (the condensate fraction) is typically  
8 separated into a wax fraction boiling in the range of about 650°F-1200°F after  
9 removing particulate catalyst fines and one or more fractions boiling above  
10 about 1200°F. The wax fraction primarily contains C<sub>20</sub> to C<sub>50</sub> linear  
11 hydrocarbons (paraffins, olefins and alcohols) with relatively small amounts of  
12 higher boiling branched hydrocarbons. Typically, the separation is effected by  
13 fractional distillation. The desired C<sub>6-8</sub> and C<sub>18-26</sub> fractions can be isolated  
14 from the condensate and liquid fractions using techniques known to those of  
15 skill in the art.

16

## Optional Process Steps

18

19 The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic  
20 contaminants in the feedstock is undesirable. For this reason, it is preferred  
21 to remove sulfur and other contaminants from the feed before performing the  
22 Fischer-Tropsch chemistry. Means for removing these contaminants are well  
23 known to those of skill in the art. For example, ZnO guardbeds are preferred  
24 for removing sulfur impurities. Means for removing other contaminants are  
25 well known to those of skill in the art.

26

27 In one embodiment, any methane produced by the reaction is recovered and  
28 converted to synthesis gas for recycling in the process. In some  
29 embodiments, the product stream may contain a relatively large amount of  
30 olefins that can be hydrogenated following the Fischer-Tropsch chemistry.

31

-15-

1 Removal of the methane and isolation of C<sub>6-8</sub> and C<sub>18-26</sub> fractions also  
2 provides C<sub>9-17</sub> and C<sub>27+</sub> fractions. The C<sub>9-17</sub> fraction is in the diesel fuel range,  
3 and can either be used directly, or alternatively, can be isomerized to improve  
4 the pour point. Methods for isomerizing hydrocarbon feeds are well known to  
5 those of skill in the art.

6

7 The C<sub>27+</sub> fraction can either be isolated and used directly, or can be reacted  
8 to form lower molecular weight products, as desired. For example, the high  
9 molecular weight products can be hydrocracked to provide lower molecular  
10 weight products, which can be used, for example, as components in liquid  
11 combustible fuels. The C<sub>27+</sub> fraction can also be converted into lube base  
12 stocks by isomerization.

13

14 Hydrocracking refers to a catalytic process, usually carried out in the  
15 presence of free hydrogen, in which the cracking of the larger hydrocarbon  
16 molecules is a primary purpose of the operation. Desulfurization and/or  
17 denitration of the feed stock usually will also occur.

18

19 Catalysts used in carrying out hydrocracking operations are well known in the  
20 art, and it should not be necessary to describe them in detail here. See, for  
21 example, U.S. Patent Nos. 4,347,121 and 4,810,357 for general descriptions  
22 of hydrotreating, hydrocracking, and typical catalysts used in each process.  
23 The product from the hydrocracking can be subject to distillation and/or  
24 catalytic isomerization to provide lube oils, diesel fuel, and the like.

25

26 Catalytic Reforming Processes Using the C<sub>6-8</sub> Product Stream

27

28 The C<sub>6-8</sub> product stream is reformed, for example, using catalytic reforming  
29 conditions, to form aromatic products. Reforming is a complex process and  
30 involves a number of competing processes or reaction sequences. These  
31 include dehydrogenation of cyclohexanes to aromatics, dehydroisomerization  
32 of alkylcyclopentanes to aromatics, dehydrocyclization of acyclic

-16-

1 hydrocarbons to aromatics, and hydrocracking of paraffins to light products  
2 boiling outside the gasoline range. In addition, the dealkylation of  
3 alkylbenzenes and the isomerization of paraffins occur in reforming  
4 processes. As the C<sub>6-8</sub> product stream includes predominantly acyclic  
5 hydrocarbons, the major reforming reaction is dehydrocyclization.

6

7 Conditions suitable for reforming C<sub>6-8</sub> product streams are well known in the  
8 art, and include the AROMAX® Process and platforming or rheniforming  
9 processes. The AROMAX® Process is well known to those of skill in the art,  
10 and is described, for example, in *Petroleum & Petrochemical International*,  
11 Volume 12, No. 12, pages 65 to 68, as well as U.S. Patent No. 4,456,527 to  
12 Buss et al., the contents of which are hereby incorporated by reference.

13

14 These processes, their commercial startup conditions, and their useful range  
15 of process operating conditions are all well known to those skilled in the art.  
16 These processes can be carried out in a single reactor or in a series of  
17 reactors.

18

19       Feedstock

20

21 The C<sub>6-8</sub> fraction includes normal paraffins and alpha olefins and a minimum  
22 of isoparaffins, and is used as at least a portion of the feedstock for the  
23 catalytic reforming reaction. Isoparaffins can participate in the reaction if they  
24 are not too highly branched, for example, like 2,2-dimethylbutane and  
25 2,3-dimethylbutane. Accordingly, mono-alkylparaffins such as  
26 mono-methylparaffins can be present in the feedstock. Several di- and  
27 poly-alkylparaffins can also be present since they are relatively non-reactive  
28 under the reaction conditions. Preferably, the stream includes predominantly  
29 C<sub>6</sub> and C<sub>7</sub> hydrocarbons. Using the AROMAX® Process, yields of aromatic  
30 compounds are nearly 90% when this stream is used.

31

-17-

1 As with the Fischer-Tropsch reaction described above, the feed should be  
2 substantially free of sulfur, nitrogen, metals and other known poisons.  
3 Methods for removing such poisons from the feed have been discussed  
4 above. In a preferred embodiment, the C<sub>6</sub>-8 hydrocarbons contacting the  
5 catalyst are substantially dry and free of sulfur, i.e., sulfur levels are preferably  
6 maintained below about 50 ppb, preferably below about 25 ppb, and more  
7 preferably below about 10 ppb. Sulfur removal systems are well known in the  
8 ultra-low sulfur reforming art. If the product of the Fischer-Tropsch reaction in  
9 the C<sub>6</sub>-8 range is combined with other feedstocks in that range, sulfur and  
10 other impurities need to be removed.

11

12       Conversion Processes

13

14 The catalytic reforming process is a low sulfur reforming process, preferably  
15 using a bound, halided Pt L-zeolite catalyst. Catalytic reforming is well  
16 known. For example, it is described in the book, *Catalytic Reforming*, by  
17 D. M. Little, PennWell Books (1985), which is incorporated herein by  
18 reference in its entirety.

19 The reaction is preferably conducted at a temperature between 400°F and  
20 1100°F, more preferably between 800°F and 1050°F. In the temperature  
21 range of from 400°C to 600°C, the catalytic reforming reaction can occur with  
22 acceptable speed and selectivity. When using traditional reforming catalysts,  
23 if the operating temperature is below 400°C, the reaction speed is insufficient  
24 and consequently the yield is too low for industrial purposes. When the  
25 operating temperature is above 600°C, interfering secondary reactions such  
26 as hydrocracking and coking may occur, reducing the yield. These secondary  
27 reactions are minimized using the bound, halided, zeolite catalysts described  
28 herein. They can also be minimized by incorporating an alkali metal, such as  
29 potassium, or an alkaline earth metal, such as barium, strontium or calcium,  
30 preferably barium, into the catalysts. The metals can be incorporated, for

-18-

1 example, via ion exchange, as described, for example, in U.S. Patent  
2 No. 4,447,316 to Buss et al., the contents of which are hereby incorporated by  
3 reference.

4

5 The pressure is preferably between 0 and 400 psig, more preferably between  
6 15 and 150 psig. The recycle hydrogen rate is sufficient to yield a hydrogen  
7 to hydrocarbon mole ratio for the feed to the reforming reaction zone between  
8 0.1 and 20, more preferably between 0.5 and 10, and most preferably  
9 between 2 and 6. The liquid hourly space velocity (LHSV) for the  
10 hydrocarbon feed over the reforming catalyst is between 0.1 and 10 hr<sup>-1</sup>, more  
11 preferably between 0.5 and 5 hr<sup>-1</sup>. Reforming produces hydrogen. Thus,  
12 additional hydrogen is not needed except when the catalyst is reduced upon  
13 startup, and when the feed is first introduced. Once reforming is underway,  
14 part of the hydrogen that is produced is preferably recycled over the catalyst.

15

16 In one embodiment, aromatics are prepared by first preparing a halided  
17 zeolite catalyst, bringing the catalyst on stream using commercial startup  
18 conditions, and contacting the catalyst with the C<sub>6-8</sub> paraffinic fraction at  
19 catalytic reforming conditions to produce aromatics. The catalyst is preferably  
20 prepared by washing a calcined, bound zeolite catalyst base with an aqueous  
21 liquid, and adding at least one halogen-containing compound and a Group VIII  
22 metal compound to the washed base.

23

24 In a preferred embodiment, the C<sub>6-8</sub> fraction is converted to an aromatic  
25 product stream by catalytic conversion of the C<sub>6-8</sub> feed under conversion  
26 conditions that include a commercial-type catalyst startup (at a low gas flow  
27 rate and a slow heat-up rate). The process preferably uses a bound and  
28 washed halided zeolite catalyst containing a Group VIII metal, where the  
29 halided catalyst has a cycle length of >1200 hr following startup. The halided  
30 catalyst is preferably prepared by a process that involves washing a bound  
31 zeolite catalyst base or catalyst before halide addition and before reduction.

32

-19-

1    The feed can be contacted with the catalyst in a fixed bed system, a moving  
2    bed system, a fluidized system, or a batch system. Either a fixed bed system  
3    or a moving bed system is preferred. In a fixed bed system, the preheated  
4    feed is passed into at least one reactor that contains a fixed bed of the  
5    catalyst. The flow of the feed can be upward, downward or radial. The  
6    effluent from the catalytic reforming reaction zone can be separated into the  
7    desired streams or fractions.

8

9                Catalyst Selection

10

11    The catalysts used in the AROMAX® Process or similar catalytic reforming  
12    processes are preferably bound and include a Group VIII metal, preferably Pt.  
13    The catalysts are also preferably halided, and, more preferably, are (water)  
14    washed, bound, halided catalysts. The term "catalyst" includes both the final  
15    catalyst as well as precursors of the final catalyst. Precursors of the final  
16    catalyst include, for example, the calcined form of the catalyst containing the  
17    catalytic metal and also the catalyst prior to activation by reduction. As used  
18    herein, the term "bound" is intended to describe a zeolite, binder combination  
19    that is formed into aggregates such as pellets, pills, extrudates and the like.  
20    The term "catalyst base", as used herein, refers to a bound zeolite.

21

22                Zeolites

23

24    Catalysts useful in the reforming reaction typically include one or more  
25    zeolites or non-zeolitic molecular sieves and at least one catalytic metal,  
26    preferably a Group VIII metal. The catalysts typically also include a binder  
27    such as a refractory oxide, e.g., silica, alumina, chlorided alumina or silica-  
28    alumina. Preferred zeolites and/or molecular sieves are selected from those  
29    of the large and intermediate pore variety. The AROMAX® Process  
30    traditionally uses PtBaK/L-zeolite as a catalyst. Traditional platforming and  
31    rheniforming processes use Pt/Al<sub>2</sub>O<sub>3</sub> or PtRe/ Al<sub>2</sub>O<sub>3</sub> as the catalyst. These

-20-

1 and other catalysts and suitable reforming conditions are described, for  
2 example, in U.S. Patent Nos. 3,546,102; 3,574,092; 3,679,575; 4,018,711;  
3 4,104,320; 4,347,394; 4,370,224; 4,417,083; 4,434,311; 4,447,316 and  
4 5,559,068.

5

6 Catalysts including platinum on chlorinated-alumina supports and Pt-X on  
7 alumina or chlorinated-alumina supports, where X is rhenium, iridium or tin  
8 have been used in catalytic reforming reactions. U.S. Pat. No. 4,370,224  
9 discloses a multi-metallic reforming catalyst that includes platinum, iridium,  
10 copper, selenium and halogen, composited with an inorganic oxide support or  
11 carrier, preferably alumina. Zeolite-containing reforming catalysts, for  
12 example, the zeolite mordenite, ZSM-type zeolites, zeolite L, Faujasites X and  
13 Y, and the zeolite omega have been used.

14

15 Representative of the large pore zeolites are ZSM-3, ZSM-4, ZSM-10,  
16 ZSM-12, ZSM-20, zeolite beta, zeolite omega, zeolite L, zeolite X, zeolite Y,  
17 REY, USY, RE-USY, mordenite, LZ-210, LZ-210-M, LZ-210-T, LZ-210-A,  
18 SSZ-24, SSZ-26, SSZ-31, SSZ-33, SSZ-35, SSZ-37, SSZ-41, SSZ-42,  
19 SSZ-44 and MCM-58. ZSM-3 is described in U.S. Patent No. 3,415,736.  
20 ZSM-4 is described in UK Application No. 1,117,568. ZSM-10 is described in  
21 U.S. Patent No. 3,692,470. ZSM-12 is described in U.S. Patent  
22 No. 3,832,449. ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite  
23 beta is described in U.S. Patent No. Re. 28,341 (of original U.S. Patent  
24 No. 3,308,069). Zeolite omega is described in U.S. Patent No. 4,241,036.  
25 Zeolite L is described in U.S. Patent No. 3,216,789. Zeolite X is described in  
26 U.S. Patent No. 2,882,244. Zeolite Y is described in U.S. Patent  
27 No. 3,130,007. LZ-210, LZ-210-M, LZ-210-T, LZ-210-A and mixtures thereof  
28 are described in U.S. Patent No. 4,534,853. SSZ-24 is described in U.S.  
29 Patent No. 4,834,977. SSZ-26 is described in U.S. Patent No. 4,910,006.  
30 SSZ-31 is described in U.S. Patent No. 5,106,801. SSZ-33 is described in  
31 U.S. Patent No. 4,963,337. SSZ-35 is described in U.S. Patent  
32 No. 5,316,753. SSZ-37 is described in U.S. Patent No. 5,254,514. SSZ-41 is

-21-

1 described in U.S. Patent No. 5,591,421. SSZ-42 is described in U.S. Serial  
2 No. 08/199,040. SSZ-44 is described in U.S. Patent No. 5,580,540. MCM-58  
3 is described in U.S. Patent No. 5,437,855. The entire contents of all these  
4 patents and patent applications are incorporated herein by reference.

5

6 Preferably, the catalyst is an L-zeolite or a zeolite having an L-zeolite-type  
7 channel structure and size, such as ECR-2 which is described in U.S. Patent  
8 No. 4,552,731, and ECR-31 which is described in U.S. Patent No. 5,624,657  
9 (Vaughan). Preferably, the catalyst is a monofunctional, non-acidic K  
10 L-zeolite. Acidity in the L-zeolite generally leads to poor performance in  
11 catalytic reforming. Examples of useful L-zeolites include those described in  
12 U.S. Patent Nos. 3,216,789 (Breck), 4,552,731 (Vaughan), 4,544,539  
13 (Wortel), 5,491,119 (Verduijn), and 4,530,824 (assigned to Tosoh Ltd.). The  
14 entire contents of all these patents are incorporated herein by reference. One  
15 useful non-acidic L-zeolite is manufactured by Union Oil Product (UOP),  
16 Mobile, AL. A preferred non-acidic L-zeolite is manufactured by Tosoh Ltd.,  
17 Japan, and sold under the name HSZ-500KOA. For these non-acidic zeolites,  
18 potassium is a preferred cation; a preferred catalyst comprises K L-zeolite.

19 Preferred catalysts are monofunctional. They do not have the acid function of  
20 conventional reforming catalysts. In contrast, conventional reforming  
21 catalysts are bifunctional, with an acid and a metal function. Examples of  
22 monofunctional catalysts include platinum on L-zeolite, wherein the L-zeolite  
23 has been exchanged with an alkali metal, as disclosed in U.S. Patent  
24 No. 4,104,320 to Bernard et al.; platinum on L-zeolite, wherein the L-zeolite  
25 has been exchanged with an alkaline earth metal, as disclosed in U.S. Patent  
26 No. 4,634,518 to Buss and Hughes; and platinum on L-zeolite as disclosed in  
27 U.S. Patent No. 4,456,527 to Buss, Field and Robinson. The entire contents  
28 of all these patents are incorporated herein by reference.

29

30 The term "non-acidic" is understood by those skilled in this area of art,  
31 particularly by the contrast between monofunctional (non-acidic) reforming

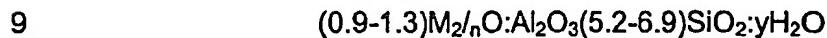
-22-

1 catalysts and bifunctional (acidic) reforming catalysts. One method of  
2 achieving non-acidity is by replacing protons with alkali and/or alkaline earth  
3 metals in the zeolite. This is preferably achieved, along with other catalyst  
4 enhancements, by an ion exchange process on the synthesized zeolite.

5

6 The composition of type L-zeolite expressed in terms of mole ratios of oxides,  
7 may be represented by the following formula:

8



10

11 In the above formula, M represents a cation, n represents the valence of M,  
12 and y may be any value from 0 to about 9. Zeolite L, its X-ray diffraction  
13 pattern, its properties, and method for its preparation are described in detail  
14 in, for example, U.S. Patent No. 3,216,789, the contents of which is hereby  
15 incorporated by reference. The actual formula may vary without changing the  
16 crystalline structure. For example, the mole ratio of silicon to aluminum (Si/Al)  
17 may vary from 1.0 to 3.5.

18

19 As discussed above, one preferred embodiment of the invention uses  
20 monofunctional Pt L-zeolite catalysts that have been treated with halogen-  
21 containing compounds. This type of halogen treatment is known. For  
22 example, U.S. Patent No. 5,091,351 to Murakawa et al. discloses preparing a  
23 Pt L-zeolite catalyst, and then treating it with a halogen-containing compound.  
24 Other related patents that disclose halided L-zeolite catalysts include  
25 EP 498,182A or U.S. Patent No. 5,354,933, which discloses co-impregnation  
26 of an L-zeolite with NH<sub>4</sub>Cl and NH<sub>4</sub>F; U.S. Patent Nos. 4,681,865, 4,761,512  
27 and 5,073,652 to Katsuno et al. These patents are all incorporated herein by  
28 reference. One preferred hiz-cat for catalytic reforming comprises halided  
29 platinum K L-zeolite catalyst, especially one containing both chloride and  
30 fluoride.

31

-23-

1 Examples of useful intermediate pore size zeolites include ZSM-5, ZSM-11,  
2 ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SUZ-4, SSZ-23; SSZ-25,  
3 SSZ-28, SSZ-32 and SSZ-36. ZSM-5 is described in U.S. Patent  
4 No. Re. 29,948 (of original U.S. Patent No. 3,702,886). ZSM-11 is described  
5 in U.S. Patent No. 3,709,979. ZSM-22 is described in U.S. Patent  
6 No. 4,556,477. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35  
7 is described in U.S. Patent No. 4,016,245. ZSM-48 is described in U.S.  
8 Patent No. 4,585,747. SUZ-4 is described in EP Application No. 353,915.  
9 SSZ-23 is described in U.S. Patent No. 4,859,422. SSZ-25 is described in  
10 U.S. Patent Nos. 4,827,667 and 5,202,014. SSZ-28 is described in U.S.  
11 Patent No. 5,200,377. SSZ-32 is described in U.S. Patent No. 5,053,373.  
12 SSZ-36 is described in U.S. Serial No. 60/034,252. The entire contents of all  
13 these patents and patent applications are incorporated herein by reference.

14

15 In addition to silicon, the useful zeolites herein can contain one or more  
16 framework elements other than, or in addition to, aluminum, e.g., the  
17 borosilicate zeolites. Also, the zeolites can be modified to alter their  
18 as-synthesized framework silica to alumina ratio.

19

20 Suitable catalysts can also include non-zeolitic molecular sieves with  
21 intermediate or large size pores. Non-zeolitic molecular sieves are  
22 microporous compositions that are formed from  $[AlO_2]$  and  $[PO_2]$  tetrahedra  
23 and have electrovalently neutral frameworks. See U.S. Patent No. 4,861,743.

24 Also included among the useful zeolites are materials of similar structure or  
25 behavior, e.g., crystalline metallophosphates such as those described in U.S.  
26 Patent No. 4,440,871. Non-zeolitic molecular sieves include  
27 aluminophosphates ( $AlPO_4$ ) as described for example in U.S. Patent  
28 No. 4,310,440, metalloaluminophosphates as described in U.S. Patent  
29 Nos. 4,500,651; 4,567,029; 4,544,143; and 4,686,093, and non-metal  
30 substituted aluminophosphates as described in U.S. Patent No. 4,973,785.

31

-24-

1 Useful catalysts also include intermediate pore silicoaluminophosphates  
2 (SAPO's) as the non-zeolitic molecular sieve component. Intermediate pore  
3 SAPO's include SAPO-11, SAPO-31, SAPO-41 and SM-3. U.S. Patent  
4 No. 4,440,871 describes SAPO's generally and SAPO-11, SAPO-31 and  
5 SAPO-41 specifically. The preparation of SM-3 and its unique characteristics  
6 are described in U.S. Patent No. 5,158,665. All these patents are  
7 incorporated herein by reference.

8

## **Binders**

10

11 The zeolites and/or molecular sieves are bound. They are preferably  
12 composited with matrix materials resistant to the temperatures and other  
13 conditions employed in hydrocarbon conversion processes. Such matrix  
14 materials can include active and inactive materials. Frequently, binders, such  
15 as naturally occurring clays and inorganic oxides, are added to improve the  
16 crush strength of the catalyst. The selection of binders and binding conditions  
17 depends on the zeolite and its intended use.

18

19 Suitable binder materials include synthetic or naturally occurring zeolites,  
20 alumina, clays such as montmorillonite and kaolin, and the refractory oxides  
21 of metals of Groups IVA and IVB of the Periodic Table of the Elements.

Particularly useful are the oxides of silicon, titanium and zirconium, with silica being preferred, especially low acidity silica. Combinations of such oxides with other oxides are also useful, for example, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, titania-zirconia, silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. These oxides can be crystalline or amorphous, or can be in the form of gelatinous precipitates, colloids, sols, or gels. Silica in the form of a silica sol is a preferred binder. A preferred silica sol has about 30 wt. % silica and contains small particles (7-9 nm in diameter), which result in catalysts with good attrition resistance and excellent crush strengths.

32

1 Extrusion aids and viscosity modifiers are generally used in addition to the  
2 binders for forming pellets or extrudates from zeolites and/or molecular  
3 sieves. These additives are typically organic compounds such as cellulose  
4 based materials, for example, Methocel® sold by Dow Chemical Co., ethylene  
5 glycol, and stearic acid. Many such compounds are known in the art. These  
6 additives should not leave a detrimental residue, i.e., one with undesirable  
7 reactivity or one that can block pores, after calcination. Preferably, the  
8 residues do not add significant amounts of alkali or alkaline earth ash to the  
9 catalyst. The above-described washing will remove low levels of these  
10 materials. The residue from the extrusion aid is preferably less than a few  
11 tenths of a percent by weight, more preferably less than 0.1 wt. %.

12

13 Methods for preparing catalyst compositions are well known to those skilled in  
14 the art and include such conventional techniques as spray drying, pelletizing,  
15 extrusion, various sphere-making techniques and the like. The methods of  
16 in-extrudate formation of the zeolite/binder described in U.S. Patent  
17 No. 5,558,851 to Miller and in U.S. Patent No. 5,514,362 can also be used.  
18 The entire contents of these patents are incorporated herein by reference.

19

20 The relative proportions of zeolite to the binder/matrix can vary widely.  
21 Generally, the zeolite content ranges from between about 1 to about 99 wt. %,  
22 and more usually in the range of from about 5 to about 95 wt. %, of the dry  
23 composite, more typically 50-85 wt. %.

24

25 Preferably, whole extrudates rather than crushed extrudates or unbound  
26 zeolites are used. Bound zeolites reduce the pressure drop through a reactor,  
27 provide improved flow rates, and are easier to load and unload. However, the  
28 diffusion characteristics of whole extrudates are quite different from those of  
29 unbound powdered zeolites. The interaction of a diffusing gas, such as a  
30 halocarbon, is different for a powdered versus a bound zeolite. Diffusion  
31 differences would also be especially significant if the catalyst evolves  
32 materials such as gases or solids, for example during startup. Moreover, the

-26-

1 act of binding itself — including selecting binding materials and the binding  
2 method — as well as calcining can affect catalyst performance. For example,  
3 the binder can interact with the sieve by simply blocking internal and external  
4 sites or by chemical interaction (e.g., alkali from a basic sieve like the  
5 preferred L-zeolite of the present invention and silica are known to react under  
6 thermal and hydrothermal calcination conditions). Moreover, the distribution  
7 of impregnated materials may vary considerably on zeolite powder versus  
8 bound zeolites. Thus, studies on powders alone cannot be used to predict  
9 commercial performance of bound zeolite catalysts.

10

### **Group VIII Metal**

12

13 The catalyst preferably includes at least one Group VIII metal, preferably a  
14 noble metal (Pt, Pd, Rh, Ir, Ru, Os), and more preferably platinum. Group VIII  
15 metal promoters; such as tin, germanium, cobalt, nickel, and combinations  
16 thereof can also be used. Preferred amounts of metal are 0.1 to 5 wt. %,  
17 more preferably 0.1 to 3 wt. %, and most preferably 0.3 to 1.5 wt. %, based on  
18 the L-zeolite. Platinum compounds that form positively charged platinum  
19 complex ions in solution are the preferred source of platinum. Platinum  
20 tetraammine chloride and nitrate are especially preferred.

21

22 Additionally, one or more non-platinum group metals such as tin, indium and  
23 Group VIIB metals such as rhenium can be added. Examples include Pt/Sn,  
24 Pt/Pd, Pt/Ni, and Pt/Re. These metals can be readily introduced into the  
25 composite employing a variety of known and conventional techniques, e.g.,  
26 ion-exchange, incipient wetness, pore fill, impregnation, etc. Care should be  
27 taken so that the Group VIII metal, e.g., platinum, is incorporated in a manner  
28 that results in excellent and uniform dispersion. The incipient wetness  
29 impregnation method is preferred.

30

1

Halides

2

3 The catalysts are preferably "hiz-cats," also referred to herein as "halided  
4 catalysts" or "halided zeolite catalysts". The term "hiz-cat" is intended to  
5 include zeolite catalysts that result from adding halogen-containing  
6 compounds to, or from halide impregnation of, zeolites, catalyst bases (i.e.,  
7 bound zeolites) or zeolite catalysts (i.e., zeolites containing catalytic metal).  
8 The halides of the hiz-cats are in addition to those that may be incorporated  
9 into the catalyst from the catalytic metal source; that is, this halogen addition  
10 or impregnation is not just that associated with conventional platinum loading  
11 and impregnation, where platinum halides are often used. Nor does this  
12 halogen treatment include conventional zeolite ion exchange operations.  
13 Zeolite ion exchange sometimes uses a halide salt, such as KCl, to replace  
14 the cations in the zeolite; this ion exchange can leave small amounts of halide  
15 on the catalyst. Moreover, the term hiz-cat is not intended to include catalysts  
16 where halide is added using alkali halides (e.g., KCl) or alkaline earth halides.  
17 Added alkali is believed to be detrimental to hiz-cats performance.

18

19 The form in which the halide is present in hiz-cats is unknown, and may be as  
20 ionic halide, neutral halide, or it may be part of a compound, such as a silica  
21 halide or Pt halide. The term "halide" is used in a broad sense, and is not  
22 intended to denote the ionic state of the added halogen or of the halogen  
23 associated with the catalyst.

24

25 The halide can be chloride, fluoride, bromide, iodide, or combinations thereof.  
26 Preferably, the hiz-cat contains chloride and/or fluoride, more preferably both.  
27 Especially preferred hiz-cats can be prepared by treating the bound zeolite or  
28 bound catalyst with halocarbons such as freons or with other chlorine-  
29 containing and/or fluorine-containing compounds, e.g., by impregnation with  
30 ammonium chloride and ammonium fluoride. Preferred hiz-cats useful in this  
31 invention have high total halide after calcination (this includes all halides, e.g.,  
32 both chloride and fluoride), i.e., they contain at least about 0.9 wt. % halide,

-28-

1 preferably at least about 1.1 wt. %, and more preferably at least about  
2 1.3 wt. % total combined halide. More than about 5 wt. % halide does not  
3 appear to provide significant advantages. When chloride and fluoride are  
4 both present, the weight ratio of Cl to F can vary. Preferably, it is between  
5 1:10 and 10:1. More preferably, chloride and fluoride are added in a weight  
6 ratio of about 1:1.

7

8 The terms "chloride retensivity" and "retained chloride" denote the residual  
9 chloride content of the catalyst after dry-out, reduction and about 300 hr  
10 on-stream. Hiz-cats evolve chloride during these steps, especially during  
11 reduction. Thereafter, the chloride level on the catalyst remains substantially  
12 constant as the catalyst is brought on-stream and operated. After startup,  
13 some halide does continue to evolve, but very slowly. Care should be taken  
14 not to overheat the catalyst, (i.e., temperatures above about 950°F) since  
15 additional chloride will evolve, and this overheating is not desirable.

16

17 Bound hiz-cat performance can be significantly improved by washing, for  
18 example, with water, before the halide is added. Preferred catalysts retain  
19 less of the added chloride than poor catalysts, even though the retained  
20 chloride, i.e., the "chloride retensivity" is independent of startup conditions.  
21 The sodium content of preferred catalysts is about 0.4 wt. %. Preferred  
22 catalysts include less than about 0.5 wt. %, more preferably less than  
23 0.45 wt. %, and most preferably less than 0.4 wt. % chloride.

24

25 Hiz-Cat Preparation

26

27 Hiz-cats can be prepared by extruding and then washing either the bound  
28 catalyst or the catalyst base before halide addition. Preferably, the catalyst is  
29 prepared by:

30

31 (a) preparing a calcined silica-bound zeolite catalyst base;

-29-

- 1    (b)    washing the bound zeolite catalyst base with an aqueous liquid; and  
2  
3    (c)    incorporating a group VIII metal and halogen-containing compound(s)  
4       comprising chlorine and fluorine into the washed base to produce a  
5       halided zeolite catalyst.

6

7    Preferably, the catalyst is prepared using a low alkali, e.g., low sodium,  
8       extrusion aid in step (a). The Pt and halogen-containing compounds can be  
9       incorporated sequentially or, preferably, simultaneously. A calcined catalyst  
10      base is preferably washed before adding the halogen-containing compounds  
11      and the Group VIII metal, e.g., platinum. In this way, these added  
12      components are not washed out of the catalyst. The catalyst base is  
13      preferably washed with one or more volumes of wash water. The washing  
14      desirably removes at least 20%, preferably at least 50%, of the readily  
15      removable alkali.

16

17   Catalyst performance can also be improved by various ion exchange  
18   processes. Cation exchange, such as with potassium and the like, often  
19   includes a wash step. Hiz-cat performance is improved when the ion  
20   exchange includes a wash step.

21

22                  Isolation of Aromatic Products

23

24   Benzene, toluene and C<sub>8</sub> aromatic streams (i.e., xylenes and ethylbenzene)  
25   can be recovered using conventional techniques such as distillation and  
26   extraction.

27

28                  Alkylation of the Aromatic Products

29

30   The alkylation of aromatics, as described herein, involves reaction of olefins  
31   with aromatic rings in the presence of an acid catalyst. The reaction is similar  
32   to Friedel-Crafts alkylation chemistry, except that an olefin, rather than a

-30-

1      haloalkane, is used to alkylate the aromatic rings. While C<sub>18-26</sub> is the preferred  
2      range of alkyl groups for the alkylation reaction, in some embodiments, it may  
3      be desired to prepare other alkylbenzenes where the alkyl groups have  
4      different molecular weight ranges, for example, C<sub>9-17</sub> or C<sub>27-50</sub>. The processes  
5      described herein are also intended to include these embodiments.

6

7      The feedstock for the alkylation reaction as described herein is the C<sub>18-26</sub>  
8      fraction isolated from a Fischer-Tropsch reaction, which is mostly paraffinic. If  
9      there are significant sulfur or solid impurities, these should be removed.  
10     Moderate amounts of linear olefins (<40 mol. %) can be tolerated, as well as  
11     linear alcohols (<40 mol. %). Both of these are capable of alkylating an  
12     aromatic ring.

13

14     The paraffinic C<sub>18-26</sub> fraction must be converted into olefins, for example, via  
15     dehydrogenation chemistry.

16

17     Catalysts and conditions for the dehydrogenation of alkanes to form olefins  
18     are well known to those of skill in the art and are described, for example, in  
19     U.S. Patent No. 3,445,541 to Heckelsberg et al., U.S. Patent No. 3,856,876 to  
20     Burnett, U.S. Patent No. 4,148,833 to Antos, U.S. Patent No. 4,420,649 to  
21     Antos, U.S. Patent No. 4,476,344 to Kimble, U.S. Patent No. 4,827,066 to  
22     Herber et al., U.S. Patent No. 4,482,646 to Eastman, U.S. Patent  
23     No. 4,686,316 to Morrison, U.S. Patent No. 4,7516,342 to Kimble, U.S. Patent  
24     No. 4,777,319 to Kung, U.S. Patent No. 4,778,942 to Vora et al., U.S. Patent  
25     No. 4,798,911 to Lentz et al., U.S. Patent No. 4,827,066 to Herber et al., U.S.  
26     Patent No. 4,827,072 to Imai et al., U.S. Patent No. 4,880,764 to Imai et al.,  
27     U.S. Patent No. 4,897,253 to Jenkins, U.S. Patent No. 4,929,792 to Dessau,  
28     U.S. Patent No. 4,956,517 to Johnson et al., U.S. Patent No. 4,973,779 to  
29     Imai et al., U.S. Patent No. 4,982,047 to Barri et al., U.S. Patent  
30     No. 5,012,027 to Abrevaya et al., U.S. Patent No. 5,143,886 to Iezzi et al.,  
31     U.S. Patent No. 5,308,822 to Iezzi et al., U.S. Patent No. 5,321,192 to Cottrell  
32     et al., U.S. Patent No. 5,430,220 to Khare et al., U.S. Patent No. 5,563,314 to

-31-

1 Agaskar et al., U.S. Patent No. 5,633,421 to Iezzi et al., U.S. Patent  
2 No. 5,905,180 to Yokoyama et al., U.S. Patent No. 5,972,203 to Smith et al.,  
3 European Patent Application 0 558 148 A1, and European Patent Application  
4 0 560 437 A1, the contents of each of which are hereby incorporated by  
5 reference.

6

7 Suitable dehydrogenation catalysts typically include a Group VIII metal from  
8 the Periodic Table of the Elements, which includes iron, cobalt, nickel,  
9 palladium, platinum, rhodium, ruthenium, osmium and iridium.

10

11 Platinum and palladium or the compounds thereof are preferred for use as  
12 dehydrogenation catalysts, with platinum and compounds thereof being  
13 especially preferred. When referring to a particular metal in this disclosure as  
14 being useful, the metal may be present as an elemental metal or as a  
15 compound of the metal. Reference to a particular metal is not intended to  
16 limit the invention to any particular form of the metal unless the specific name  
17 of the compound is given, as in the examples in which specific compounds  
18 are named as being used in the preparations.

19

20 The process conditions selected for carrying out the dehydrogenation step will  
21 depend upon the dehydrogenation catalyst used. In general, the pressure is  
22 usually the lowest pressure consistent with the maintenance of catalyst  
23 stability. The pressure is typically in the range of between about 0.1 and  
24 10 atm, preferably between about 0.5 and 3 atm. The temperature is typically  
25 between about 700°C to about 1200°F, with temperatures in the range of  
26 between 800°F and 950°F being particularly preferred. The LHSV is typically  
27 between 1 and 40 hr<sup>-1</sup>, preferably between about 25 and 35 hr<sup>-1</sup>. In the event  
28 the catalyst deactivates with the time-on-stream, specific processes that are  
29 well known to those skilled in art are available for the regeneration of the  
30 catalysts. Any number of reactors for the dehydrogenation and alkylation

1 steps can be used, such as fixed bed, fluidized bed, ebulated bed, and the  
2 like.

3

4 The dehydrogenation and alkylation reactions can occur in the same reactor,  
5 since the presence of aromatics is not detrimental to the dehydrogenation  
6 reaction. In this embodiment, the aromatic fraction and the C<sub>18-26</sub> fraction are  
7 combined in a single reactor that includes a dehydrogenation catalyst and an  
8 alkylation catalyst. However, the product of the reaction may include alkyl  
9 chains with more than one aromatic ring, resulting from dehydrogenation and  
10 alkylation of the alkyl chain on the alkylbenzenes. For this reason, it can be  
11 preferred to perform the dehydrogenation and alkylation reactions in separate  
12 reactors, and, optionally, to remove any di-olefins from the olefin stream used  
13 in the alkylation step.

14

15 The UOP Pacol and Detal processes are well-known process for alkylating  
16 aromatics using a dehydrogenation catalyst (Pacol) and an alkylation catalyst  
17 (Detal). These processes are described, for example, in Vora et al.,  
18 Chemistry and Industry, 187-191 (1990), the contents of which are hereby  
19 incorporated by reference. In the Pacol process, the conversion of n-paraffins  
20 to mono-olefins is near equilibrium. A relatively small amount of the  
21 n-paraffins is converted to di-olefins and aromatics. In the alkylation step,  
22 diolefins produce di-phenylalkanes or heavier polymers, which tends to lower  
23 the overall product yield. However, the amount of diolefins can be minimized,  
24 for example, using the UOP DeFine process. The DeFine process is a  
25 selective hydrogenation process that converts di-olefins to mono-olefins.

26

27 In a preferred embodiment, alkyl groups are subjected to dehydrogenation  
28 conditions to form a product stream containing a mixture of unconverted  
29 n-paraffins, mono-olefins and di-olefins. The product stream is reacted with a  
30 selective catalyst to hydrogenate the di-olefins to mono-olefins. The  
31 unconverted n-paraffins and mono-olefins are sent to a separate reactor along  
32 with the aromatics. The preferred ratio of aromatics to olefins is between

-33-

1 about 2 and 50, preferably between 5 and 20. An alkylation catalyst, typically  
2 a strong acid catalyst such as HF, sulfuric acid, an acidic ionic liquid such as a  
3 quaternary amine-chloroaluminate salt, or an acidic zeolite catalyst, is used to  
4 alkylate the aromatics. An example of an alkylation reaction is the UOP Detal  
5 process.

6

7 Typically, the reaction products include unconverted paraffins, unconverted  
8 aromatics, alkylbenzenes, heavy alkylate (aromatics with more than one alkyl  
9 group) and polymers (formed from the acid-catalyzed polymerization of  
10 olefins). The aromatics and unconverted paraffins can be obtained via  
11 fractional distillation and recycled. The product can be separated from the  
12 heavy alkylate via fractional distillation.

13

14 Additional details on the UOP Pacol, De Fine and Detal processes are  
15 described, for example, in Schultz et al., "LAB Production, Second World  
16 Conference on Detergents", Montreux, Switzerland, Oct. 5-19, 1986;  
17 "Handbook of Petroleum Refining Processes," ed. R. Myers, New York,  
18 McGraw-Hill, 1986; Vora et al., "Production of biodegradable detergent  
19 intermediates," Second World Surfactants Congress, Paris, France,  
20 May 24-27 (1988); and Broughton, "Adsorptive separations - liquids" in  
21 "Kirk-Othmer Encyclopedia of Chemical Technology," Vol. 1, 3rd ed., New  
22 York, John Wiley & Sons, 1978, the contents of which are hereby  
23 incorporated by reference. Additional examples of alkylation chemistry are  
24 described, for example, in EPA 0 731 072 by Chevron Chemical SA.

25

26 The resulting alkylbenzenes can be used directly, for example, as synthetic  
27 lubricants (synlubes) and/or detergents in a variety of applications, for  
28 example, as lubricant oils. Alternatively, they can be sulfonated to form  
29 surfactants, or hydrogenated to form alkylcyclohexanes, which are useful in  
30 synthetic lube oil compositions.

31

-34-

1           Hydrogenation of Alkylbenzenes to form Alkylcyclohexanes

2

3   Conditions for hydrogenating benzene rings to form cyclohexane rings are  
4   well known to those of skill in the art. Care must be taken to avoid  
5   hydrocracking conditions, which might strip the alkyl groups from the ring.

6

7   Suitable catalysts and conditions for hydrogenating aromatic rings without  
8   removing the alkyl side chains are well known in the art. Typical catalysts are  
9   palladium or platinum catalysts on alumina or silica/alumina supports,  
10   although ruthenium and rhodium catalysts can also be used. The reactions  
11   are typically performed at a temperature between about 200°F and 500°F,  
12   preferably around 300°F, under a hydrogen atmosphere at a pressure of  
13   between about 100 and 500 psig.

14

15           Sulfonation of Alkylbenzenes to form sulfonated alkylbenzenes

16

17   Conditions for sulfonating alkylbenzenes are well known to those of skill in the  
18   art and are described, for example, in EPA 0 731 072 by Chevron Chemical  
19   SA, the contents of which are hereby incorporated by reference. In  
20   EPA 0 731 072, alkylbenzenes are sulfonated by first forming sulfuric  
21   anhydride, and then reacting the alkylbenzene with the sulfuric anhydride.

22   Sulfuric anhydride is formed by oxidizing sulfur dioxide at 450°C in the  
23   presence of a vanadium oxide catalyst. The sulfonation reaction takes place  
24   in a tube maintained at 65°C by falling film, where the sulfuric anhydride is  
25   diluted with nitrogen and the alkylbenzene/sulfur dioxide ratio is maintained at  
26   about 1.05. Residual sulfuric acid is then eliminated by thermal treatment  
27   after dilution with about 10% of 100N oil, bubbling through nitrogen at the rate  
28   of about 10 l/h/kg of product and agitating at 85°C, until a lower residual  
29   sulfuric acid content is obtained (typically less than about 0.5%). The  
30   resulting sulfonated alkylbenzenes can be used, for example, as detergents  
31   and/or dispersants.

-35-

1        Lube Oil Compositions

2

3     The alkylcyclohexanes formed from the hydrogenation of the alkylbenzenes  
4     are useful as lube oils or as components in lube oil compositions. The lube oil  
5     compositions preferably have a kinematic viscosity of at least 3 centistokes,  
6     more preferably at least 4 centistokes, still more preferably at least  
7     5 centistokes, and most preferably at least 6 centistokes, where the viscosity  
8     is measured at 40°C. They also have a viscosity index (a measure of the  
9     resistance of viscosity change to changes in temperature) of at least 100,  
10    preferably 140 or more, more preferably over 150, and most preferably over  
11    160.

12

13    Another important property for the lube oil compositions is that they have a  
14    relatively high flash point for safety reasons. Preferably, the flash point is  
15    above 90°C, more preferably above 110°C, still more preferably greater than  
16    175°C, and most preferably between 175°C and 300°C. The following table  
17    (Table 1) shows a correlation between viscosity and flash point of preferred  
18    lubricants for use in automobiles.

19

20

Table 1

Viscosity at 40°C (cSt)	Flash Point (D93), °C	Flash Point (D92), °C
3.0	175	175
4.08	205	208
4.18	201	214
6.93	230	237
11.03	251	269

21

22    \*D92 and D93 listed in the above table refer to ASTM tests for measuring  
23    flash point:

24

25    Flash Point, COC, °C      D 92  
26    Flash Point, PMCC, °C      D 93

27

-36-

1 The lube oil can be used, for example, in automobiles. The presence of the  
2 aromatic or cyclohexane rings on the long alkyl chains gives it relatively high  
3 additive solubility (the ability to dissolve lube oil additives) and seal swell  
4 performance, relative to lube oils that do not include the aromatic or  
5 cyclohexane rings. Seal swell (the ability to adsorb in gaskets that line the  
6 lubricating system, causing them to swell slightly and make a good seal) is  
7 higher for the alkylbenzenes and alkylcyclohexanes described herein than for  
8 paraffinic lube oils that do not include these rings.

9

10 The lube oil can also be used as a blending component with other oils. This  
11 can be particularly important when a lube oil includes alkylbenzenes of  
12 alkylcyclohexanes in combination with pure paraffinic oils, where the  
13 combination provides increased additive solubility and seal swell  
14 characteristics. For example, the lube oil can be used as a blending  
15 component with polyalphaolefins, or with mineral oils to improve the viscosity  
16 and viscosity index properties of those oils, or can be combined with  
17 isomerized petroleum wax. The lube oils can also be used as workover fluids,  
18 packer fluids, coring fluids, completion fluids, and in other oil field and well-  
19 servicing applications. For example, they can be used as spotting fluids to  
20 unstick a drill pipe that has become stuck, or they can be used to replace part  
21 or all of the expensive polyalphaolefin lubricating additives in downhole  
22 applications. Additionally, they can also be used in drilling fluid formulations  
23 where shale-swelling inhibition is important, such as those described in U.S.  
24 Pat. No. 4,941,981 to Perricone et al.

25

#### Optional Components

27

28 The lube oil compositions include the alkylcyclohexanes, optionally include  
29 conventional lubricants, and preferably also include various additives, such as  
30 lubricants, emulsifiers, wetting agents, densifiers, fluid-loss additives, viscosity  
31 modifiers, corrosion inhibitors, oxidation inhibitors, friction modifiers,  
32 demulsifiers, anti-wear agents, dispersants, anti-foaming agents, pour point

1 depressants, detergents, rust inhibitors and the like. Other hydrocarbons,  
2 such as those described in U.S. Patent No. 5,096,883 and/or U.S. Patent  
3 No. 5,189,012, may be blended with the lube oil provided that the final blend  
4 has the necessary pour point, kinematic viscosity, flash point, and toxicity  
5 properties. The total amount of additives is preferably between 1-30 percent.  
6 All percentages listed herein are weight percentages unless otherwise stated.

7

8 Examples of suitable lubricants include polyol esters of C<sub>12</sub>-C<sub>28</sub> acids.

9

10 Examples of viscosity modifying agents include polymers such as ethylene  
11 alpha-olefin copolymers which generally have weight average molecular  
12 weights of from about 10,000 to 1,000,000 as determined by gel permeation  
13 chromatography.

14

15 Examples of suitable corrosion inhibitors include phosphosulfurized  
16 hydrocarbons and the products obtained by reacting a phosphosulfurized  
17 hydrocarbon with an alkaline earth metal oxide or hydroxide.

18

19 Examples of oxidation inhibitors include antioxidants such as alkaline earth  
20 metal salts of alkylphenol thioesters having preferably C<sub>5</sub>-C<sub>12</sub> alkyl side chain  
21 such as calcium nonylphenol sulfide, barium t-octylphenol sulfide,  
22 dioctylphenylamine, as well as sulfurized or phosphosulfurized hydrocarbons.  
23 Additional examples include oil soluble antioxidant copper compounds such  
24 as copper salts of C<sub>10</sub> to C<sub>18</sub> oil soluble fatty acids.

25

26 Examples of friction modifiers include fatty acid esters and amides, glycerol  
27 esters of dimerized fatty acids and succinate esters or metal salts thereof.

28

29 Dispersants are well known in the lubricating oil field and include high  
30 molecular weight alkyl succinimides being the reaction products of oil soluble  
31 polyisobutylene succinic anhydride with ethylene amines such as  
32 tetraethylene pentamine and borated salts thereof.

- 1 Pour point depressants such as C<sub>8</sub>-C<sub>18</sub> dialkyl fumarate vinyl acetate
- 2 copolymers, polymethacrylates and wax naphthalene are well known to those
- 3 of skill in the art.
- 4
- 5 Examples of anti-foaming agents include polysiloxanes such as silicone oil
- 6 and polydimethyl siloxane; acrylate polymers are also suitable.
- 7
- 8 Examples of anti-wear agents include zinc dialkyldithiophosphate, zinc diaryl
- 9 diphosphate, and sulfurized isobutylene.
- 10
- 11 Examples of detergents and metal rust inhibitors include the metal salts of
- 12 sulfonic acids, alkylphenols, sulfurized alkylphenols, alkyl salicylates,
- 13 naphthenates and other oil soluble mono and dicarboxylic acids such as
- 14 tetrapropyl succinic anhydride. Neutral or highly basic metal salts such as
- 15 highly basic alkaline earth metal sulfonates (especially calcium and
- 16 magnesium salts) are frequently used as such detergents. Also useful is
- 17 nonylphenol sulfide. Similar materials made by reacting an alkylphenol with
- 18 commercial sulfur dichlorides. Suitable alkylphenol sulfides can also be
- 19 prepared by reacting alkylphenols with elemental sulfur. Also suitable as
- 20 detergents are neutral and basic salts of phenols, generally known as
- 21 phenates, wherein the phenol is generally an alkyl substituted phenolic group,
- 22 where the substituent is an aliphatic hydrocarbon group having about 4 to
- 23 400 carbon atoms.
- 24
- 25 Antioxidants can be added to the lube oil to neutralize or minimize oil
- 26 degradation chemistry. Examples of antioxidants include those described in
- 27 U.S. Pat. No. 5,200,101, which discloses certain amine/hindered phenol, acid
- 28 anhydride and thiol ester-derived products.
- 29
- 30 The combination of a metallic dithiophosphate hydroperoxide decomposer
- 31 and aminic antioxidant is reported to have a synergistic effect on lubricant
- 32 antioxidant performance. See Maleville et al., *Lubrication Science*, V9, No. 1,

-39-

1 pp. 3-60 (1996). Sulfur-substituted derivatives of mercapto carboxylic esters  
2 also are reported to possess antioxidant properties. See M. A. Mirozopeva  
3 et al., *Naftekhimiya*, V28, No. 6, pp. 831-837 (1988).

4

5 Additional lube oils additives are described in U.S. Patent No. 5,898,023 to  
6 Francisco et al., the contents of which are hereby incorporated by reference.

7

8 The process will be readily understood by referring to the flow diagram in  
9 Figure 1. In Figure 1, a mixture of carbon monoxide and hydrogen (syngas) is  
10 added to a Fischer-Tropsch reactor (Box 10). A C<sub>6-8</sub> fraction and a C<sub>18-26</sub>  
11 fraction are separately isolated via distillation (Box 20). The C<sub>6-8</sub> fraction is  
12 subjected to catalytic reforming to form aromatics and hydrogen gas (Box 30)  
13 and the C<sub>18-26</sub> fraction is dehydrogenated to form linear alpha olefins (Box 40).  
14 The linear alpha olefins are used to alkylate the aromatics (Box 50), and the  
15 resulting alkylbenzene compounds are optionally hydrogenated to form  
16 alkylcyclohexanes (Box 60). In the flow scheme contained in Figure 1, the  
17 process of the present invention is practiced in continuous operation.  
18 However, it is possible to practice the present invention in batch operation.

-40-

1    WHAT IS CLAIMED IS:

2

3    1. An integrated process for preparing alkylbenzenes, the process  
4       comprising;

5

6       (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a

7              hydrocarbon product stream comprising olefins and paraffins;

8

9       (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the  
10              product stream;

11

12       (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic  
13              reforming conditions to form C<sub>6-8</sub> aromatics;

14

15       (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to  
16              dehydrogenation conditions; and

17

18       (e) alkylating the C<sub>6-8</sub> aromatics with olefins in the C<sub>18-26</sub> fraction.

19

20    2. The process of claim 1, wherein the Fischer-Tropsch reaction conditions  
21       are such that the fraction rich in C<sub>6-8</sub> hydrocarbons is obtained from a  
22       reaction where the catalyst provides low to moderate chain growth  
23       probabilities.

24

25    3. The process of claim 2, wherein the catalyst comprises iron.

26

27    4. The process of claim 1, wherein the Fischer-Tropsch reaction conditions  
28       are such that the fraction rich in C<sub>18-26</sub> hydrocarbons is obtained from a  
29       reaction where the catalyst provides high chain growth probabilities.

30

31    5. The process of claim 4, wherein the catalyst comprises cobalt.

32

-41-

- 1     6. The process of claim 1, wherein the catalytic reforming step is performed
- 2                 using the AROMAX® Process.
- 3
- 4     7. The process of claim 1, wherein the catalytic reforming step is performed
- 5                 using platforming or rheniforming processes.
- 6
- 7     8. The process of claim 1, wherein the dehydrogenation catalyst includes at
- 8                 least one metal or a corresponding metal compound selected from the
- 9                 group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium,
- 10                 osmium, iridium and platinum.
- 11
- 12    9. The process of claim 1, wherein the dehydrogenation catalyst
- 13                 component comprises a noble metal or a compound thereof.
- 14
- 15    10. The process of claim 9, wherein the noble metal is platinum or palladium
- 16                 or a mixture of platinum and palladium or the compounds thereof.
- 17
- 18    11. The process of claim 9, wherein the dehydrogenation/hydrogenation
- 19                 component also contains rhenium or a compound of rhenium.
- 20
- 21    12. The process of claim 1, further comprising isolating unreacted C<sub>18-26</sub>
- 22                 paraffins from the alkylation step, subjecting them to dehydrogenation
- 23                 conditions, and recycling them in the alkylation step.
- 24
- 25    13. The process of claim 1, wherein the alkylation reaction is performed
- 26                 using the Detal process.
- 27
- 28    14. The process of claim 1, wherein the aromatics used in the alkylation step
- 29                 further comprise aromatics not derived from the fraction rich in C<sub>6-8</sub>
- 30                 hydrocarbons from the product stream in the Fischer-Tropsch step.
- 31

-42-

1    15. The process of claim 1, wherein the C<sub>18-26</sub> olefins used in the alkylation  
2    step further comprise C<sub>18-26</sub> olefins which are not derived from the  
3    fraction rich in C<sub>18-26</sub> hydrocarbons from the product stream in the  
4    Fischer-Tropsch step.

5

6    16. An alkylbenzene composition obtained by the steps of:

7

8        (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a  
9                      hydrocarbon product stream comprising olefins and paraffins;

10      (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the  
11                      product stream;

12

13      (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic  
14                      reforming conditions to form C<sub>6-8</sub> aromatics;

15

16      (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to  
17                      dehydrogenation conditions; and

18

19      (e) alkylating the C<sub>6-8</sub> aromatics with olefins in the C<sub>18-26</sub> fraction to  
20                      form alkylbenzenes.

21

22    17. An integrated process for preparing alkylcyclohexanes, the process  
23                      comprising;

24

25        (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a  
26                      hydrocarbon product stream comprising olefins and paraffins;

27

28        (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the  
29                      product stream;

30

-43-

- 1       (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic
- 2              reforming conditions to form C<sub>6-8</sub> aromatics;
- 3
- 4       (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to
- 5              dehydrogenation conditions;
- 6
- 7       (e) alkylating the C<sub>6-8</sub> aromatics with olefins in the C<sub>18-26</sub> fraction to
- 8              form alkylbenzenes; and
- 9
- 10      (f) hydrogenating the alkylbenzenes to form alkylcyclohexanes.
- 11
- 12     18. The process of claim 17, wherein the Fischer-Tropsch reaction
- 13              conditions are such that the fraction rich in C<sub>6-8</sub> hydrocarbons is obtained
- 14              from a reaction where the catalyst provides low to moderate chain
- 15              growth probabilities.
- 16
- 17     19. The process of claim 18, wherein the catalyst comprises iron.
- 18
- 19     20. The process of claim 17, wherein the Fischer-Tropsch reaction
- 20              conditions are such that the fraction rich in C<sub>18-26</sub> hydrocarbons is
- 21              obtained from a reaction where the catalyst provides high chain growth
- 22              probabilities.
- 23
- 24     21. The process of claim 20, wherein the catalyst comprises cobalt.
- 25
- 26     22. The process of claim 17, wherein the catalytic reforming step is
- 27              performed using the AROMAX® Process.
- 28
- 29     23. The process of claim 17, wherein the catalytic reforming step is
- 30              performed using platforming or rheniforming processes.
- 31

-44-

- 1    24. The process of claim 17, wherein the dehydrogenation catalyst includes  
2       at least one metal or a corresponding metal compound selected from the  
3       group consisting of iron, cobalt, nickel, ruthenium, rhodium, palladium,  
4       osmium, iridium and platinum.
- 5
- 6    25. The process of claim 17, wherein the dehydrogenation catalyst  
7       component comprises a noble metal or a compound thereof.
- 8
- 9    26. The process of claim 25, wherein the noble metal is platinum or  
10      palladium or a mixture of platinum and palladium or the compounds  
11      thereof.
- 12
- 13    27. The process of claim 24, wherein the dehydrogenation/hydrogenation  
14      component also contains rhenium or a compound of rhenium.
- 15
- 16    28. The process of claim 17, further comprising isolating unreacted C<sub>18-26</sub>  
17      paraffins from the alkylation step, subjecting them to dehydrogenation  
18      conditions, and recycling them in the alkylation step.
- 19
- 20    29. The process of claim 17, wherein the alkylation reaction is performed  
21      using the Detal process.
- 22
- 23    30. An alkylcyclohexane composition obtained by the steps of:  
24
- 25       (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a  
26           hydrocarbon product stream comprising olefins and paraffins;
- 27
- 28       (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the  
29           product stream;
- 30
- 31       (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic  
32           reforming conditions to form C<sub>6-8</sub> aromatics;

- 1       (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to  
2                    dehydrogenation conditions;
- 3
- 4       (e) alkylating the C<sub>6-8</sub> aromatics with the olefins in the C<sub>18-26</sub> fraction to  
5                    form alkylbenzenes; and
- 6
- 7       (f) hydrogenating the alkylbenzenes to form alkylcyclohexanes.
- 8
- 9     31. The composition of claim 30, further comprising one or more lube oil  
10           additives selected from the group consisting of lubricants, emulsifiers,  
11           wetting agents, densifiers, fluid-loss additives, viscosity modifiers,  
12           corrosion inhibitors, oxidation inhibitors, friction modifiers, demulsifiers,  
13           anti-wear agents, dispersants, anti-foaming agents, pour point  
14           depressants, detergents, and rust inhibitors.
- 15
- 16     32. A sulfonated alkylbenzene composition obtained by the steps of:  
17
- 18       (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a  
19           hydrocarbon product stream comprising olefins and paraffins;
- 20
- 21       (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the  
22           product stream;
- 23
- 24       (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic  
25           reforming conditions to form C<sub>6-8</sub> aromatics;
- 26
- 27       (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to  
28           dehydrogenation conditions;
- 29
- 30       (e) alkylating the C<sub>6-8</sub> aromatics with the olefins in the C<sub>18-26</sub> fraction to  
31           form alkylbenzenes; and
- 32

-46-

- 1           (f) sulfonating the alkylbenzenes to form sulfonated alkylbenzenes.
- 2
- 3     33. A method for enhancing the additive solubility and/or seal swell
- 4        performance of a paraffinic lube oil composition comprising adding an
- 5        effective additive solubility enhancing and/or seal swell performance
- 6        enhancing amount of an alkylcyclohexane and/or alkylbenzene
- 7        composition to the paraffinic lube oil composition.
- 8
- 9     34. The method of claim 33, wherein the alkylbenzene composition is
- 10      obtained by the steps of:
- 11
- 12       (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a
- 13        hydrocarbon product stream comprising olefins and paraffins;
- 14
- 15       (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the
- 16        product stream;
- 17
- 18       (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic
- 19        reforming conditions to form C<sub>6-8</sub> aromatics;
- 20
- 21       (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to
- 22        dehydrogenation conditions; and
- 23
- 24       (e) alkylating the C<sub>6-8</sub> aromatics with the olefins in the C<sub>18-26</sub> fraction to
- 25        form alkylbenzenes.
- 26
- 27     35. The method of claim 33, wherein the alkylcyclohexane composition is
- 28      obtained by the steps of:
- 29
- 30       (a) subjecting syngas to Fischer-Tropsch reaction conditions to form a
- 31        hydrocarbon product stream comprising olefins and paraffins;
- 32

-47-

- 1       (b) isolating fractions rich in C<sub>6-8</sub> and C<sub>18-26</sub> hydrocarbons from the
- 2              product stream;
- 3
- 4       (c) subjecting the fraction rich in C<sub>6-8</sub> hydrocarbons to catalytic
- 5              reforming conditions to form C<sub>6-8</sub> aromatics;
- 6
- 7       (d) optionally subjecting the fraction rich in C<sub>18-26</sub> hydrocarbons to
- 8              dehydrogenation conditions;
- 9
- 10      (e) alkylating the C<sub>6-8</sub> aromatics with the olefins in the C<sub>18-26</sub> fraction to
- 11              form alkylbenzenes; and
- 12
- 13      (f) hydrogenating the alkylbenzenes to form alkylcyclohexanes.

1/1

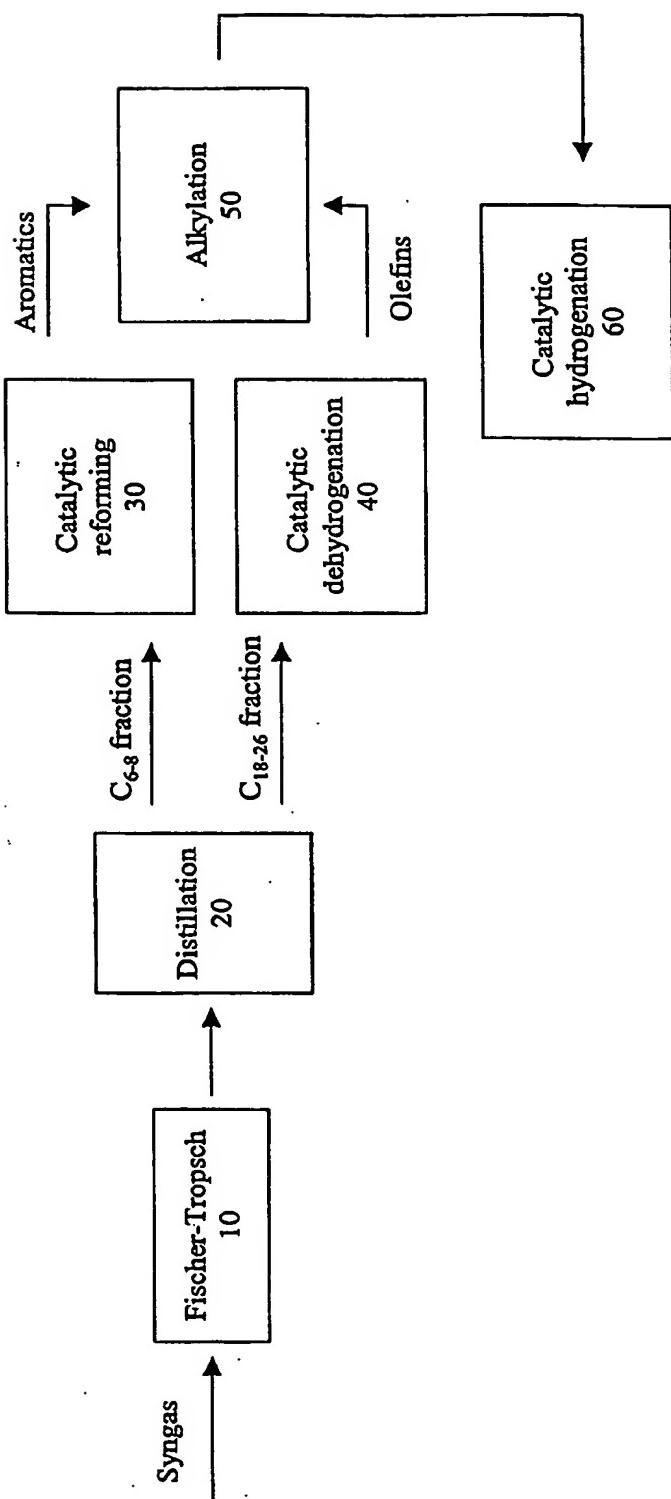


Figure 1

## INTERNATIONAL SEARCH REPORT

Inte  
al Application No  
PCT/US 01/06358

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07C15/107 C07C13/18 C07C309/31 C10M127/02 C10M127/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	WO 01 02325 A (SASOL TECHNOLOGY; DE WET EWALD WATERMEYER) 11 January 2001 (2001-01-11) claims -----	1,16
A	GB 669 313 A (CALIFORNIA RESEARCH CORP) 2 April 1952 (1952-04-02) claims -----	32

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

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1

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Inten al Application No

PCT/US 01/06358

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 0102325	A	11-01-2001	AU	6541100 A		22-01-2001
GB 669313	A	02-04-1952		NONE		